[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE, MASS.]

The Condensation of 9,10-Phenanthraquinone with Acetic Anhydride

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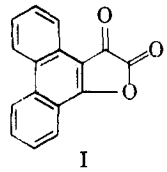
The condensation of 9,10-phenanthraquinone with acetic anhydride has been reinvestigated and the structures VI and IX assigned to the products of the reaction.

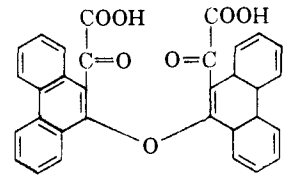
In 1905, Meyer[3] reported the synthesis of 2,3-diketo-4,5;6,7-dibenzocoumaran (I) by treatment of 9,10-phenanthraquinone with potassium hydroxide in ethanol. Later the same year Scharwin[4] described an alternative preparation of I. 9,10-Phenanthraquinone, on the steam-bath with acetic



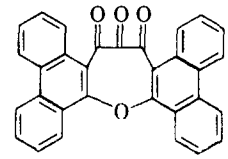
I

anhydride and sodium acetate, gave three compounds, A, B and C. Basic hydrolysis of compound A followed by acidification gave the keto-lactone I reported by Meyer. Scharwin proposed the formula $C_{33}H_{20}O_7$ for A on the basis of an analysis and a molecular weight determination. Compound B, which was intensely blue, was not examined further as the yields were quite small. Finally, Scharwin noted that C possessed the same melting point as 9,10-diacetoxyphenanthrene.

Years later Diels and Kassebart[5] published a lengthy paper in which new structural formulas were advanced for A and B as well as for several other derivatives obtained for the first time in their study. They obtained B in good yield by running the condensation of the phenanthraquinone and acetic anhydride in pyridine in the dark at room temperature. When the condensation was conducted at an elevated temperature an isomeric compound BB was obtained. Their analyses suggested the formulas $C_{32}H_{18}O_7$ and $C_{31}H_{16}O_4$ for A and B, respectively. Pyrolysis of A at 280° led to B. An impressive list of derivatives of B were made, all in agreement with the formula $C_{31}H_{16}O_4$. These included an N-methylaniline adduct, two hydrolysis products different from the keto-lactone obtained from A, and an *o*-phenylenediamine adduct. The N-methylaniline adduct, when heated in nitrobenzene, gave a new compound D, which could also be obtained directly from B on irradiation with sunlight. Analysis of D was in agreement with $C_{30}H_{16}O_3$ and the loss of carbon monoxide during the reaction was established readily. On the basis of these data and the earlier work of Scharwin on the hydrolysis of B, the structures II, III, IV and V were assigned to A, B, BB and D, respectively.



II



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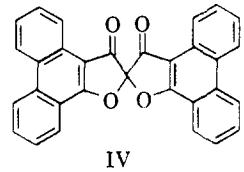
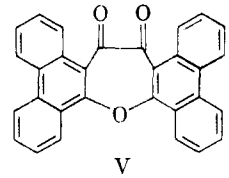
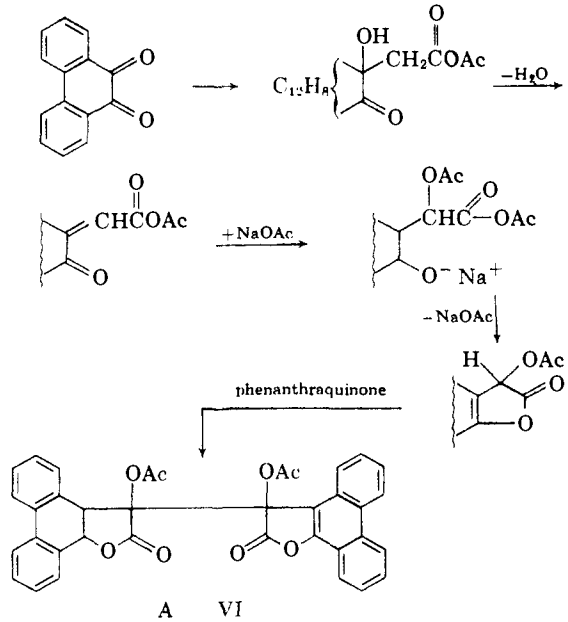


IV



V

As the structural assignments of Diels and Kassebart were difficult to deduce logically from the reactants, a reinvestigation of the problem was undertaken. The compounds in question were made as reported by Scharwin[4] and Diels.[5] The infrared spectrum of A, with carbonyl bands at 5.5 and 5.7 μ, clearly indicated the necessity of revising the earlier structural assignment. The 5.5 μ band suggested the presence of a highly strained unsaturated lactone ring in A.[6] Utilizing this idea, a new working structure for A may be obtained by a reasonable sequence of steps.



A VI

In the last step of the scheme, 9,10-phenanthraquinone is utilized as the oxidizing agent for the

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(2) General Electric Fellow 1955–1956. Abstracted from the Ph. D. Thesis of Stanley M. Bloom, Harvard University, September, 1956. The author is pleased to acknowledge with thanks the guidance of Professor R. B. Woodward during the course of this work.

(3) R. Meyer and O. Spengler, *Ber.*, **38**, 440 (1905).

(4) W. Scharwin, *ibid.*, **38**, 1270 (1905).

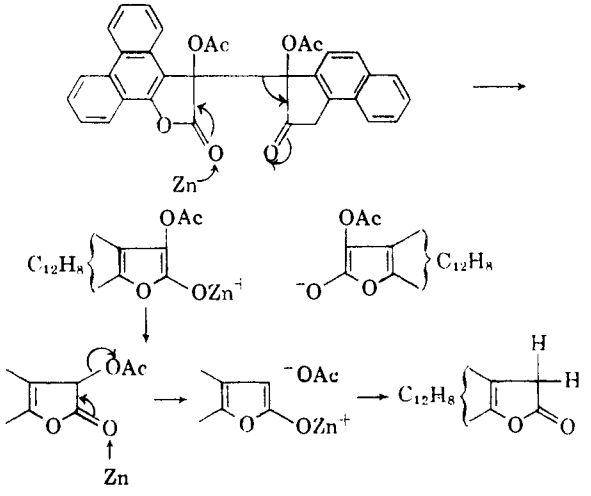
(5) O. Diels and R. Kassebart, *Ann.*, **536**, 78 (1938).

(6) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 159, and R. N. Jones, *et al.*, *Can. J. Chem.*, **37**, 2007 (1959).

dimerization, thus providing an explanation for the ready isolation of compound C, assigned to 9,10-diacetoxyphenanthrene by Scharwin.[4,7]

The change in the assigned formula for A necessitated by the proposed scheme and the subsequent changes in formulas for B, its derivatives, and D (*vide infra*) is to be noted. Although the analysis obtained for A by Diels and Kassebart was in agreement with their formulation, it is in even better agreement with the new formulation (VI). The analytical data of Diels and Kassebart for the compounds B, D, etc., are all in satisfactory agreement with the calculated values for the new formulations to be developed.

Confirmation of Scharwin's structural assignment for C was readily forthcoming. 9,10-Phenanthraquinone was reduced to the diol, acetylated and the 9,10-diacetoxyphenanthrene so synthesized was shown to be identical with C. Proof of the assignment, VI, for A then was undertaken. Zinc in acetic acid, chosen to reverse the proposed dimerization step, led to the formation of a compound, $C_{16}H_{10}O_2$, which proved to be identical with 2-keto-4,5;6,7-dibenzocoumaran (VII).[8,9]



The isolation of VII in over 50% yield is uniquely explicable by VI.[10] The new structure for A provides an explanation for the isolation of I on basic hydrolysis.

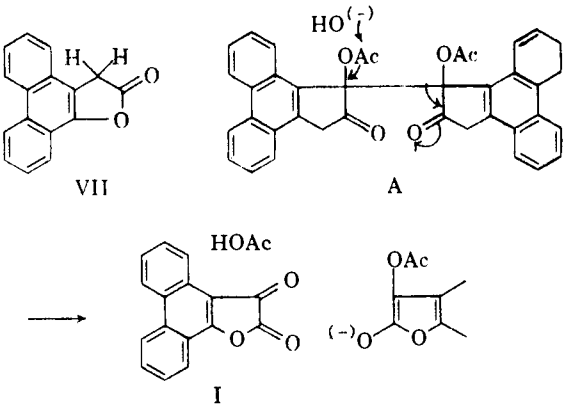
The intense indigo-like color of B, (λ_{max} 633 mμ in toluene) provided the key to its structure. The Pechmann dyes, possessing the nucleus VIII, are deeply colored and have been studied extensively.[11]

(7) An earlier example of the proposed dimerization was described by A. Lowenbein and W. Folberth, *Ber.*, **58**, 601 (1925). Lowenbein dimerized the sodium enolate of 2-keto-3-phenylcoumaran with iodine. See also H. H. Wasserman, T. C. Liu and E. R. Wasserman, *J. Am. Chem. Soc.*, **75**, 2056 (1953).

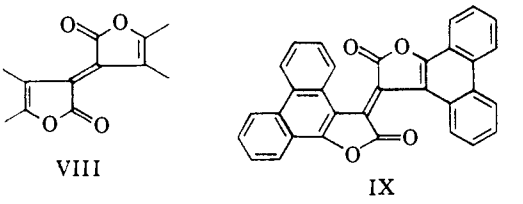
(8) The reduction may be assumed to proceed as shown although the steps may be reversed.

(9) M. B. Richards, *J. Chem. Soc.*, **97**, 1456 (1910), reported an earlier synthesis of 2-keto-4,5;6,7-dibenzocoumaran whose properties were in agreement with those of the compound isolated from the reduction. In our hands, however, the initial stage of the Richards synthesis failed. An alternate synthesis of 2-keto-4,5;6,7-dibenzocoumaran will be described below.

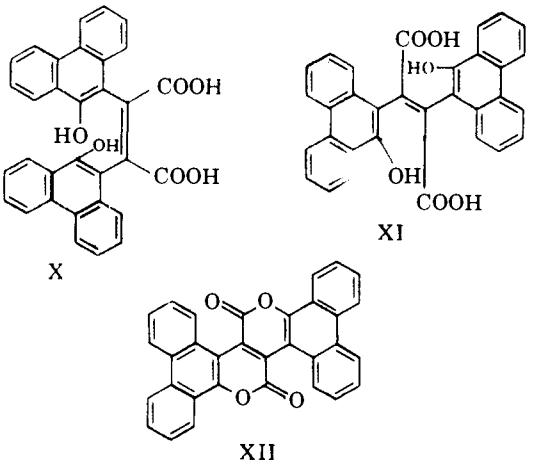
(10) A 76% yield (see Experimental section) of 2-keto-4,5;6,7-dibenzocoumaran (VII) was isolated from the reduction of A which had been shown to be dimeric earlier.[4,5] As one molecule of A gives two molecules of VII, A must contain two 4,5;6,7-dibenzocoumaran nuclei. The infrared data and the mode of reduction lead unambiguously to structure VI for A.



Loss of the equivalent of diacetyl peroxide from A on pyrolysis would lead to IX, a Pechmann dye.



To test this hypothesis IX was synthesized by a method employed earlier by Bergmann.[12] 2-Keto-4,5;6,7-dibenzocoumaran (VII) was condensed with 2,3-diketo-4,5;6,7-dibenzocoumaran (I) to give IX which proved to be identical with B. The hydrolysis products of B may be reformulated as the *cis*- and *trans*-dicarboxylic acids X and XI, a transformation commonly observed with other Pechmann dyes.[11]



The structure XII may be assigned to the compound BB, obtained from the condensation of phenanthraquinone and acetic anhydride with pyridine at elevated temperature. The assignment for BB, isomeric with B, is supported by its reported isolation from the dehydration of one of the hydrolysis products of B with acetic anhydride.[5] It is the thermodynamically more stable di-lactone.

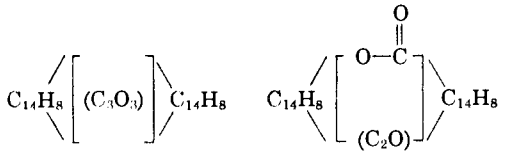
There remained only the question of the structure of D whose corrected formula is $C_{31}H_{16}O_3$.[13] An in-

(11) See E. Klingsberg, *Chem. Revs.*, **54**, 59 (1954).

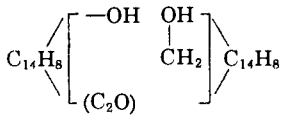
(12) C. S. Fang and W. Bergmann, *J. Org. Chem.*, **16**, 1231 (1951).

(13) The new formula for D is obtained by subtracting the carbon monoxide unit from the corrected structure of C.

frared spectrum showed no hydroxyl absorption and a single carbonyl band at 5.76 μ. Reduction with lithium aluminum hydride gave a compound, $C_{31}H_{20}O_3$, which on acetylation gave a diacetate, $C_{35}H_{24}O_5$. Examination of the infrared spectrum of the diacetate indicated the presence of phenolic and aliphatic acetate groups, for carbonyl bands were found at 5.64 and 5.78 μ. Sufficient data had been accumulated to derive a structure for D. At the outset D may be written with the partial structure XIIIa. Addition of four hydrogen atoms on reaction with lithium aluminum hydride points to the reduction of a lactone. The presence of a phenolic acetate group in the diacetate necessitates the attachment of one hydroxyl to a phenanthrene nucleus. The diol derived from D may be represented as XIV and D as XIIIb.



XIIIa XIIIb

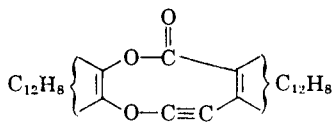


XIV

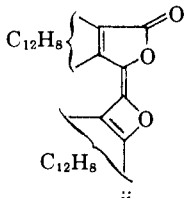
The absorption band at 5.76 μ in D can be attributed only to a lactone ring with a unit of unsaturation alpha, beta to the carbonyl grouping allowing extension of XIIIb to XIIIc.[14] Of the five structures for D derivable from XIIIc only two need be considered.[15] While a choice between D_a and D_b cannot be made with certainty, a consideration of its mode of formation from the N-methylaniline adduct will allow a tentative choice of D_a over D_b. Before examining this transformation the structure XVa will be assigned to the adduct on the basis of the following data. Firstly, the presence of a free hydroxyl was established earlier by Diels and Kassebart by the isolation of an acetate on acetylation of the adduct.[5] Secondly, the infrared spectrum of B has its carbonyl band at 5.72 μ (lactone) while the N-methylaniline adduct has carbonyl peaks at 5.79

(14) See L. J. Bellamy, ref. 6, p. 155.

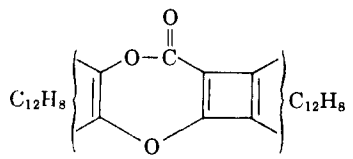
(15) The three structures i, ii and iii were discarded because of their obvious instability.



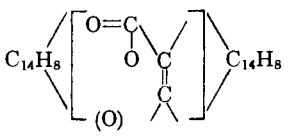
i



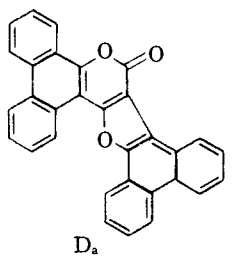
ii



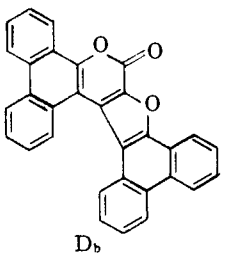
iii



XIIIc

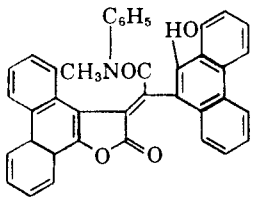


D_a

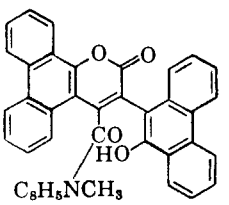


D_b

μ (lactone) and 6.15 μ (amide). The shift in the absorption points to a lactone ring less strained than that in B and eliminates XVb.

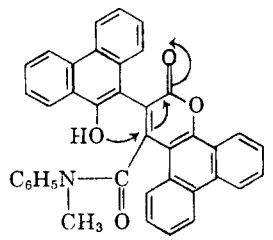


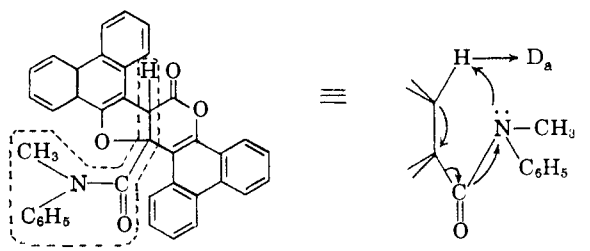
XVb



XVa

The reaction of XVa in boiling nitrobenzene may now be detailed.





D_a is obtained simply by this hypothetical route and therefore is the favored structure for D.

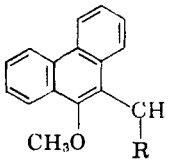
The 2-keto-4,5;6,7-dibenzocoumaran needed for this study was synthesized from 9-phenanthrol which was converted to the methyl ether[16] and then formylated[17] by procedures previously described. The 9-formyl-10-methoxyphenanthrene (XVIa) was reduced to the alcohol XVIb and transformed into the chloride XVIc. The chloride was further transformed to the nitrile XVId which on treat-

(16) The method of T. S. Stevens and S. H. Tucker, *J. Chem. Soc.*, **123**, 2140 (1923), was employed.

(17) I. M. Hunsberger, R. Ketcham and H. S. Gutowsky, *J. Am. Chem. Soc.*, **74**, 4839 (1952).

ment with aqueous hydrogen iodide in acetic acid gave the desired lactone VII.

A second synthesis of B (IX) was uncovered during the course of this work. Controlled oxidation of 2-keto-4,5;6,7-dibenzocoumaran (VII) with selenium dioxide gave a virtually quantitative yield of the Pechmann dye IX.



XVIa, R = =O
b, R = —H/OH
c, R = —H/Cl
d, R = —H/CN

Experimental[18]

Zinc Reduction of Compound A.—Compound A (541 mg.) was refluxed in acetic acid (25 ml.). Zinc dust (1.0 g.) was added over a period of an hour and the reaction refluxed 10 hours. The hot solution was decanted from the remaining solids which were washed with acetic acid, the washings being added to the decanted solution. The crude reaction product, obtained by precipitation from water, weight 330 mg., m.p. 168–170°, was recrystallized twice from ethanol–benzene under nitrogen. The analytical sample melted from 176–177°. As one mole of B on reduction leads to two moles of the isolated coumaran, a 76% yield was obtained. An infrared spectrum revealed a single carbonyl peak at 5.53 μ.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.12; H, 4.59.

Aqueous Hydrolysis of the Zinc Reduction Product.—The $C_{16}H_{10}O_2$ compound (330 mg.) was warmed on the steam-bath in 10% potassium hydroxide solution (10 ml.) until a clear solution was obtained. Cold dilute hydrochloric acid was added to precipitate the product which was washed with water before drying. The solid, weight 330 mg., was crystallized from acetone–benzene, m.p. 188.0–188.5°. Richards[9] reported a melting point of 183° for 9-hydroxy-10-phenanthrylacetic acid.

Lithium Aluminum Hydride Reduction of Compound D.—Compound D (200 mg.), tetrahydrofuran (20 ml.) and a large molar excess of lithium aluminum hydride were refluxed 8 hours. After cooling, the remaining lithium aluminum hydride was decomposed by dropwise addition of ethyl acetate. Cold water and finally hydrochloric acid were added to the tetrahydrofuran solution to decompose insoluble lithium salts. The acidified solution was extracted with three portions of chloroform which were combined, washed with water and dried. After removal of the solvent at the water aspirator the residue was crystallized from ethanol–ethyl acetate (Norite). The reduction product, weight 129 mg., was obtained as fine white needles melting over 300°. The compound was twice further crystallized from ethanol–ethyl acetate for analysis. An infrared absorption spectrum showed hydroxyl absorption at 2.93 μ but no carbonyl absorption.

Anal. Calcd. for $C_{31}H_{20}O_3$: C, 84.54; H, 4.58. Found: C, 84.43; H, 4.68.

The Diacetate of the Lithium Aluminum Hydride Reduction Product.—The $C_{31}H_{20}O_3$ compound (44 mg.), acetic anhydride (0.5 ml.) and a trace of anhydrous sodium acetate were refluxed 2 hours and the acetic anhydride was then removed at the water aspirator. Chloroform was added to dissolve the product which was filtered from the insoluble sodium acetate. On removal of the solvent and scratching, the residue crystallized. The compound was recrystallized twice from ethyl acetate–cyclohexane; m.p. 228.0–228.5°. An infrared spectrum showed carbonyl absorption (dichloromethane) at 5.64 and 5.78 μ.

Anal. Calcd. for $C_{35}H_{24}O_6$: C, 80.14; H, 4.61. Found: C, 80.44; H, 4.85.

9-Chloromethyl-10-methoxyphenanthraquinone.—9-Formyl-10-methoxyphenanthraquinone[17] (2.5 g.) was dissolved in methanol (75 ml.) and sodium borohydride (2.5 g.) was added to the above solution slowly with external cooling. After refluxing for 0.5 hour the solution was filtered and the filtrate diluted to a total volume of 200 ml. with water. The desired 9-hydroxymethyl-10-methoxyphenanthrene (2.1 g., 84%), m.p. 80–85°, came down on standing in the cold room. The compound on recrystallization from carbon tetrachloride and cyclohexane–benzene melted from 88–90°. The crude 9-hydroxymethyl-10-methoxyphenanthrene (1.95 g.), m.p. 80–85°, pyridine (20 drops) and thionyl chloride (10 ml.), which was previously chilled, were allowed to react for 2.5 hours at room temperature. Nitrogen was passed through the reaction to expell hydrogen chloride and sulfur dioxide. The solution on evaporation at the water aspirator gave the product which was crystallized from ethyl acetate (Norite). 9-Chloromethyl-10-methoxyphenanthrene, 1.15 g., m.p. 113–115°, was obtained. A second crop was obtained through the addition of cyclohexane to the mother liquor. For analysis the compound was passed through a short column of Merck alumina employing benzene as eluant. Purification was completed by crystallization from ethyl acetate–cyclohexane and sublimation, m.p. 124–125°.

Anal. Calcd. for $C_{16}H_{13}OCl$: C, 74.85; H, 5.10; Cl, 13.81. Found: C, 74.53; H, 5.15; Cl, 14.05.

9-(10-Methoxyphenanthrene)-acetonitrile.—9-Chloromethyl-10-methoxyphenanthrene (1.35 g.), m.p. 113–115°, was dissolved in acetone (65 ml.). Potassium cyanide (2.6 g.) was added and the solution brought to a gentle reflux. Water was added dropwise until the refluxing solution was homogeneous and the period of reflux extended to 7 hours. After cooling, the acetone was removed at the water aspirator, and chloroform used to extract the product. The chloroform extract was washed with water, dried and taken to dryness. The 9-(10-methoxyphenanthrene)-acetonitrile obtained was crystallized from cyclohexane–benzene; 1.0 g., m.p. 148–151° (72.5%). For analysis the compound was dissolved in chloroform, washed with dilute base and recovered as before. On recrystallization from cyclohexane–benzene three times and sublimation the compound melted from 158–159.5°.

Anal. Calcd. for $C_{17}H_{13}ON$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.05; H, 5.34; N, 5.83.

2-Keto-4,5;6,7-dibenzocoumaran.—9-(10-Methoxyphenanthrene)-acetonitrile (109 mg.), hydriodic acid (50%, 2 ml.), acetic acid (4 ml.) and water (1 ml.) were refluxed for 3.5 hours. Sodium bisulfite and water were added to the hot solution and the lactone precipitated with water. On washing and drying, 89 mg., m.p. 145–159° (90%), was obtained. The lactone was crystallized from benzene–ethanol (1:1) previously treated with sulfur dioxide. After three such crystallizations the compound melted from 175–176.5°. A mixture melting point of the synthetic 2-keto-4,5;6,7-dibenzocoumaran with the C_{16}-compound obtained from the reaction of zinc in acetic acid on compound B showed no depression. Infrared spectra taken under identical conditions were virtually superimposable.

2,3-Diketo-4,5;6,7-dibenzocoumaran.—The procedure of Meyer[3] was modified. Phenanthraquinone (5 g.) and potassium hydroxide (15 g.) were refluxed for 8 hr., air being bubbled through the solution for the first half-hour. The dark brown solution obtained was allowed to stand overnight. The ethanol solution was concentrated at the water aspirator, poured into boiling water (300 ml.) and then filtered through Filter-cel. The filtrate was heated, dilute sulfuric acid added, and the precipitate collected, washed and dried. The solid was crystallized from acetone (Norite); weight 1.16 g. On recrystallization the orange 2,3-diketo-4,5;6,7-dibenzocoumaran melted with decomposition at 220–221° (Meyer[3] reported a m.p. of 220–221°).

The Synthesis of Compound B. Method A.—2-Keto-4,5;6,7-dibenzocoumaran (51 mg.) and 2,3-diketo-4,5;6,7-dibenzocoumaran (48 mg.) were refluxed in acetic anhydride (2 ml.) and acetic acid (2 drops). After 6 hr. reflux under nitrogen, the reaction was allowed to stand overnight. The solution was filtered and the precipitate washed with ethyl ether to eliminate white and green impurities. The dark glistening solid remaining, weight 40.2 mg. (41%), was crystalline as shown by examination under a polarizing microscope. The compound was further purified by washing with hot formic acid and by Soxhlet extraction with benzene until

(18) All melting points are corrected. Infrared spectra were determined in potassium iodide unless an alternate medium is mentioned.

the extract was colored blue. An infrared curve of the blue crystalline compound was in all respects identical to a spectrum of compound B.

Method B.—2-Keto-4,5;6,7-dibenzocoumaran (51 mg.) and selenium dioxide (28 mg.) were refluxed with acetic anhydride (3 ml.) for 4 hours. The solution quickly turned blue. The acetic anhydride was partially removed at the water aspirator and 50 mg. (100%) of a dark crystalline solid obtained. The infrared spectrum of the compound was identical in all respects with the spectrum of an authentic sample of compound B. The condensation, when run in ethanol, also led to compound B in smaller yield.

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Elimination Reactions of α-Halogenated Ketones. V.[1] Kinetics of the Bromide Ion Promoted Elimination Reaction of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

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2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) has been found to undergo a facile bromide ion-promoted elimination in solvent acetonitrile to yield only the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). Comparison of the kinetic order in salt, reaction rate and variation of reaction rate with temperature for tetraethylammonium bromide and for piperidine hydrobromide, used as the source of bromide ions, shows that only sufficiently dissociated bromide ions are capable of promoting the elimination reaction.

It has been shown in previous publications[2] that under a wide variety of conditions dehydrobromination of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) produces mainly, if not exclusively, the endocyclic unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II). This article reports such an elimination reaction promoted in acetonitrile solution by bromide ions when supplied either as tetraethylammonium bromide or as piperidine hydrobromide. The system is a convenient one to study since any concurrent substitution reaction will regenerate the bromotetralone I.

The elimination reaction promoted by the tetraethylammonium bromide was found to be kinetically first order in both bromotetralone I and in tetraethylammonium bromide. At 90.3°, reaction was capable of proceeding to at least 93% decomposition of the bromotetralone I, as measured by acid formation. From the temperature variation of the second-order coefficient, values for the frequency factor of $10^{10.9}$ and for the activation energy of 19.7 kcal./mole were obtained. Product studies lead to the isolation of a good yield of the endocyclic unsaturated ketone II.

The elimination reaction promoted by piperidine hydrobromide was found to be kinetically first order in bromotetralone I, but only an half integral order in piperidine hydrobromide was found. At 90.3°, reaction was capable of proceeding to at least 88% decomposition of the bromotetralone I as measured by acid formation. The temperature variation of the 3/2 order rate coefficient leads to values for the Arrhenius parameter A of $10^{9.5}$ and of the Arrhenius parameter E of 20.2 kcal./mole.

The actual reaction rates were in all cases considerably lower for a given concentration of piperidine hydrobromide than for an identical concentration of tetraethylammonium bromide; *e.g.*, for a salt concentration of 0.0200 M the rate is lower by a factor of about seven.

It appears that only sufficiently dissociated bromide ions are capable of promoting elimination reaction with the bromotetralone I. In this way the lower reaction rates and kinetic order in piperidine hydrobromide relative to tetraethylammonium bromide can be explained on the assumption that virtually all bromide ions in tetraethylammonium bromide are sufficiently dissociated but in piperidine hydrobromide only a small proportion of the bromide ions are in such a state. Conductivity measurements support this view of the mechanism since it has been shown that quaternary substituted ammonium salts are far more dissociated in acetonitrile solution than only partially substituted ammonium salts.[3]

The value for the Arrhenius parameter, E, for elimination reaction promoted by piperidine hydrobromide, 20.2 kcal./mole, is only slightly higher than the value for the activation energy for bromide ion promoted elimination as obtained from elimination promoted by tetraethylammonium bromide, 19.7 kcal./mole. This is consistent with the proposed view that the reaction mechanism is essentially identical for attack by both bromide salts. The Arrhenius parameter E, of 20.2 kcal./mole, will be a composite constant of the activation energy, 19.7 kcal./mole, together with a smaller contribution governed by the rate of increase in the degree of dissociation of the piperidine hydrobromide with temperature.

Analysis in terms of the various order rate coefficients throughout was carried out using their initial values since it was found that the integrated values for the first-order rate coefficients, calculated with respect to the bromotetralone I, fell steadily throughout each run for both of the bromide salts employed. It is probable that the hydrogen bromide produced participates in an equilibrium which to some extent removes bromide ions from solution with formation of HBr_2^- triple ions.

Deductions which can be made regarding the mechanism of the reaction are deferred until a

(1) For paper IV in this series see N. H. Cromwell and P. H. Hess, *J. Am. Chem. Soc.*, **83**, 1237 (1961).

(2) (a) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958); (b) **80**, 901 (1958); (c) N. H. Cromwell, R. P. Ayer and P. W. Foster, *ibid.*, **82**, 130 (1960).

(3) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144A**, 269 (1929).